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*Observation of Phase-Separated Nanometer Scale Molecular Domains in Mixed
Self-Assembled Monolayers*

by

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OBSERVATION OF PHASE-SEPARATED NANOMETER SCALE MOLECULAR DOMAINS IN MIXED SELF-ASSEMBLED MONOLAYERS

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We demonstrate the phase separation into nanometer scale domains of two-component monolayers prepared by self-assembly on gold of $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ and $\text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_{15}\text{SH}$, two similar, non-hydrogen bonding alkane thiols of identical alkyl chain length. By varying the fractions of the two components, we have learned to distinguish between domains of each molecule by scanning tunneling microscopy. These observations have important implications for both the scientific understanding of phase segregation in quasi-two-dimensional molecular mixtures and for applications of self-assembly in which the formation of spatially resolved mixed functional group surfaces is desired. Further, these observations provide a caveat with regard to the common assumption of complete mixing in multi-component self-assembled monolayers.

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Self-assembled monolayers (SAMs) are being intensively studied because their well-defined structural character provides molecular surfaces of great value for scientific studies and exploration of technological applications. In particular, realization of an ability to control precisely the placement of different functional groups on an assembly of substrate-bound flexible chains will provide opportunities to replicate important physico-chemical functions of biological surfaces and membranes (1). In this regard, recent studies have shown that changes in the nature of functional groups exposed at SAM surfaces can effect changes in protein adsorption (2) and cell growth (3). Strategies for creation of complex, multifunctional surface architectures, such as in artificial receptor sites (4), will require manipulation of exposed functional groups on the 1–100 nanometer scale. In order to develop such strategies there are two major hurdles. First, a quantitative understanding of the intrinsic phase behavior of mixed monolayers is needed. In particular, we must understand the tendency of unlike molecules to phase segregate into preferred spatial patterns on the nanometer scale; there does not appear to be any general understanding of this phenomenon at present. Second, in order to achieve this understanding, reliable experimental methods are needed for characterizing the spatial distribution of molecules on the 1–100 nm scale. In fact, in recent studies homogeneous mixing has been routinely assumed, due in large part to a lack of independent evidence to the contrary, for mixtures of terminally substituted alkane thiolates on gold and subsequently, contact angle wetting data have been interpreted on this basis (5). However, according to theoretical estimates, contact angle wetting methods would resolve domains no smaller than 0.1–1 μm (6), so even “large” domains on the nanometer scale would produce the same wetting behavior as uniform mixing. One of the premier techniques for chemical imaging is time-of-flight secondary ion mass spectroscopy (TOF-SIMS), but the current lateral resolution is limited to no smaller than 50 nm, the size of the ion beam spot. The use of scanning probe microscopies appear the most promising because these techniques have sufficient lateral resolution. To this end, we point out that void defects have been imaged using both atomic force microscopy (AFM) and scanning tunneling microscopy (STM) (7–9). In an encouraging application of AFM, it has recently been

shown that an exception to uniform mixing appears to occur for a pair of quite different molecules, of different length and functionality: an alkanic acid and a partially fluorinated alkyl ether with a terminal carboxylic acid group (10). In the latter study, the frictional response of the domains on the nm scale was used to obtain the desired contrast. There is as yet no indication of how general this technique will be, particularly since the frictional properties of various functional groups are not well understood. That quite different molecular structures might lead to phase segregation is further pointed out in recent experimental studies in which it has been observed that distinctly different chain length alkane thiolates on gold exhibit tendencies to phase segregate (11). Monte Carlo simulations support such phase segregation (12). Based on the above discussion, the results presented in this study intersect the field at the point at which it appears that no general method has been demonstrated for distinguishing molecular patterns on surfaces on the nanometer scale and no understanding has been put forward to show what limits can be expected in the relationship between molecular similarity and phase segregation in quasi-two-dimensional systems. Through the application of STM to the analysis of a variable composition series of two component SAMs of quite similar molecules, we show that STM can be used to map phase-segregation-induced molecular patterns and that even very similar molecular pairs display intrinsic tendencies to phase segregate.

In order to explore an example of phase segregation near the limits of expected molecular compatibility, we have deliberately selected a pair of molecules of very similar size, very similar intermolecular interactions, and very similar terminal functional groups. These are, $X-(CH_2)_{15}SH$, where $X-$ is CH_3- or CH_3O_2C- , alkane thiols of identical alkyl chain length where the only difference is the substitution of the terminal methyl group for a methyl ester group. A plethora of evidence has shown that the methyl group in $CH_3(CH_2)_{15}SH$ is the outermost group (13). Infrared spectroscopic evidence also suggests that for $CH_3O_2C(CH_2)_{15}SH$, the methyl group is the outermost group exposed at the surface (14). Despite these similarities, we show that these two molecules phase separate into nanometer scale domains. This calls into question the assumptions of complete mixing in multicomponent self-assembled structures.

Substrates were prepared by evaporating gold onto hot mica (temperature=340°C, pressure= $1-6 \times 10^{-7}$ torr). Self-assembled monolayers of $C_{16}H_{33}SH$ and $CH_3O_2C(CH_2)_{15}SH$ were prepared by soaking the substrate in a solution of the thiol(s) in ethanol ($1 \times 10^{-3} M$) for four days. Four solutions were used; one pure solution of each thiol and two mixed solutions using 1:3 and 3:1 molar ratios of the two thiols. At these concentrations, both thiols are completely soluble in ethanol, and the solutions are uniformly mixed. Companion samples were characterized by infrared spectroscopy, liquid drop contact angle, and ellipsometry to verify the quality and thickness of the assembled films (15).

The experiments reported here were conducted in air using a microwave-frequency-compatible Besocke beetle-style STM (16). All the samples studied were sufficiently conductive that we were able to use DC tunneling current to control the tip-sample separation. All images were recorded in constant tunneling current mode.

In Fig. 1, we show a $750 \text{Å} \times 730 \text{Å}$ area of a self-assembled monolayer of $C_{16}H_{33}SH$ on Au. Several terraces are visible as are a number of void defects in the films. The latter are evident as $\sim 2 \text{Å}$ depressions in the image. In ref. (8) similar defects were attributed to defects in the gold substrate induced by the monolayer adsorption. However, this explanation appears inconsistent with the larger defects observed by Kim and Bard (9) which would seem to be due to missing adsorbates. We consistently find defects of uniform size and shape, and favor interpreting these as defects in the thiol layer. Missing adsorbate defects should display definite depth characteristics as a function of the number of missing chains. In a rigid rod approximation, for chains tilted at $26-30^\circ$ (13-15) and occupying $\sim 21.6 \text{Å}^2$ per chain (nearest neighbor spacing of 5.0Å on a hexagonal lattice), removal of a single chain for example would produce a depression below the monolayer surface of $12-15 \text{Å}$ (depending upon the tilt azimuth) with the bottom being a CH_2 group of the chain across the defect span to the nearest chain. In general, removal of N adjacent chains would produce a depression N times as deep with an equivalent circular defect span on the order of $\sim [N \times \sqrt{21.6}] \text{Å}$ until the limiting value of the film thickness is reached ($\sim 22 \text{Å}$ for the C_{16} films). However, at

ambient temperature, because kT is significant compared to the $\text{CH}_2\text{--CH}_2$ rotational barriers, chains would be expected to relax conformationally into the void spaces and thereby increase the defect span while diminishing the depth. The smallest and most common defects we observe are $\sim 2\text{\AA}$ deep and $20\text{--}25\text{\AA}$ across in STM images. We note that the STM does not give a true height measurement as the tunneling probability is convoluted with the surface geometric structure in the constant current image contours recorded here (17). This area of effect is consistent with relaxation of neighboring chains into the space from a single missing chain. Using a simple model of conformationally relaxed chains having a slightly lower density (tending towards liquid), 12 chains would relax to give a 20\AA diameter hole of 2\AA depth. Thus, we speculate that these defects are due to conformational relaxation of no more than a small number of neighboring chains to fill the void left by a single missing chain. The significantly larger defects observed by Kim and Bard, we then attribute to a much larger number of missing molecules, which even with complete conformational chain relaxation produce hole depths on the scale of the film thickness. This is consistent with the factor of 50 shorter incubation times used by Kim and Bard for SAM preparation compared to the incubation periods used for our samples. Using short incubation times we have reproduced their results. The motion and distribution of defects in these films will be the topic of a future publication (18).

In Fig. 2, we show reflectance infrared spectra of samples of the four self-assembled monolayer compositions used in these studies. The peak due to the symmetric stretching mode of the terminal methyl groups appear at 2878 cm^{-1} for the methyl-terminated molecule and is not observed for the methyl-ester terminated molecule. The ratios of the integrated peak intensities show that the film compositions are representative of the solution concentrations chosen. The details of the infrared spectra in this region, in the chain mode/ester carbonyl region will be discussed elsewhere (19). Results of X-ray photoelectron spectroscopy also support the conclusion that each film composition is representative of the corresponding solution concentration. A perfect correspondence would imply that the surface mixture was an ideal solution, *viz.* the enthalpies of pure and mixed film phases all would be equal and the relative surface mole fractions would be driven only by the corresponding solution mole fractions.

In Figs. 3 and 4, we show STM images of mixed π monolayers of 3:1 and 1:3 mixtures of $C_{16}H_{33}SH$ and $CH_3O_2CC_{15}H_{30}SH$ on Au. Domains are present as distinguished by differing tip heights in the constant current STM images. One domain appears 1 Å higher and can be assigned to the ester molecule on the basis of the correlation of domain area coverage for the two different controlled composition mixtures. By measuring the fractional area recorded at each tip height, we have confirmed that the domain areas match the expected film compositions. It is from these typical images and hundreds of others obtained, that we infer the identity of the domains. Fig. 3 shows an image of the 1:3 mixture in which a single point defect is visible in one of the methyl domains. This feature matches those attributed to pinholes in the single component film shown in Fig. 1. We conclude that the regions of intermediate height are thus phase-separated, densely packed molecular domains of the methyl-terminated alkane thiolate. The height difference observed in the STM images does not correspond to the height difference of the molecules. This is because the STM tunneling current is determined by the local electronic state density where the electrons of the tip and surface overlap (17). This current is not necessarily representative of the molecular size. Based on molecular models and the known 26–30° chain tilt angles, the actual height difference of the molecules is ~ 1 Å. With these observations in mind, we have demonstrated that the monolayers do not represent the limiting case of an ideal solution, as discussed above. The self-interaction energies of each component are therefore inferred to be larger than the cross-interaction (20).

With regard to the origins of the formation of these domains, we consider three limiting scenarios. First, in surface-collision-controlled (kinetic) limit, solute thiol molecule would strike the surface randomly, be irreversibly adsorbed and totally immobilized on the surface. The result of this process would be a completely random statistical distribution of adsorbate molecules reflecting the solution composition. This is not observed. Second, in an equilibrium (thermodynamic) limit, after irreversible adsorption the thiol molecules would be completely mobile with respect to surface diffusion and (given sufficient time) would redistribute to form their equilibrium surface structures. A third possible (equilibrium) case would involve a completely reversible adsorption-desorption process in which the equilibrium structure of the film would ultimately be attained. However,

because of the stability of these films in pure solvent such a process is not feasible on the time scale of our experiments. All other film formation mechanisms can be represented as combinations of the above (including more complex adsorption steps such as film surface-solute pre-equilibria). It then follows, since our data show the existence of phase segregation that some equilibrium character is reflected in the film formation process and therefore the minimum free energy structure of the mixed monolayers consists of discrete molecular domains on some size scale.

In summary, we have demonstrated that even weakly interacting molecules which self-assemble can phase separate into discrete molecular domains on the nanometer scale. This calls into question the common assumption that even much more strongly interacting, *i.e.* hydrogen bonding, molecules randomly mix upon self-assembly. This aspect was never tested previously, because the methods used average over much larger surface areas. The application of STM now appears promising as a general probe to characterize nanometer scale phase segregation. This represents an important step in the use of self-assembly techniques in patterned and biomimetic architectures.

The next critical step is the unambiguous chemical identification of molecular domains via a local spectroscopy. To this end, we are currently performing AC scanning tunneling spectroscopy of these films in order to differentiate and identify the molecules comprising individual domains.

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19. A. N. Parikh, Y.-T. Tao, D. L. Allara, S. J. Stranick, P. S. Weiss, to be published.
20. We are currently performing two-dimensional lattice gas Monte Carlo simulations for reversible mixed adsorption in which the attraction between adsorbate A and adsorbate B is slightly lower than the identical A-A and B-B attractions. The resulting distributions for 100x100 lattices of adsorbates after 10^6 and more attempted steps per adsorbate show formation of small domains very similar in terms of shape and size to images such as those shown in Fig. 4.
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FIGURE CAPTIONS

1. A scanning tunneling microscope image showing a $750\text{\AA} \times 730\text{\AA}$ area of a self-assembled monolayer of $\text{C}_{16}\text{H}_{33}\text{SH}$ on Au. The image was recorded in constant current mode at a tunneling current of 2 nA and a tip bias voltage of $\sim 2\text{V}$. Several terraces are visible as area a number of pinholes in the films are evident as *ca.* 2\AA depressions in the image.
2. Infrared spectra of the pure and mixed self-assembled monolayer films for ratios of $\text{C}_{16}\text{H}_{33}\text{SH}$ to $\text{CH}_3\text{O}_2\text{CC}_{15}\text{H}_{30}\text{SH}$ on Au of: a) 1:0, b) 3:1, c) 1:3, and d) 0:1. The integrated intensity of the symmetric methyl stretching mode absorption at 2878 cm^{-1} , present only for the methyl-terminated thiol, is used to determine the fraction of the surface covered by $\text{C}_{16}\text{H}_{33}\text{SH}$.
3. A scanning tunneling microscope image showing a $350\text{\AA} \times 250\text{\AA}$ area of a self-assembled monolayer of a mixture of 25% $\text{C}_{16}\text{H}_{33}\text{SH}$ and 75% $\text{CH}_3\text{O}_2\text{CC}_{15}\text{H}_{30}\text{SH}$ on Au. The image was recorded in constant current mode at a tunneling current of 2 nA and a tip bias voltage of $\sim 2\text{V}$. By comparison with images such as the one shown in Fig. 4, we infer that the regions that appear higher in the image (red) are $\text{CH}_3\text{CO}_2\text{C}_{15}\text{H}_{30}\text{SH}$ domains, and the regions that appear lower (yellow) are $\text{C}_{16}\text{H}_{33}\text{SH}$ domains. Note the defect (blue) in the $\text{C}_{16}\text{H}_{33}\text{SH}$ domain in the lower right area of the image.
4. A scanning tunneling microscope image showing a $750\text{\AA} \times 500\text{\AA}$ area of a self-assembled monolayer of a mixture of 75% $\text{C}_{16}\text{H}_{33}\text{SH}$ and 25% $\text{CH}_3\text{O}_2\text{CC}_{15}\text{H}_{30}\text{SH}$ on Au. The image was recorded in constant current mode at a tunneling current of 2 nA and a tip bias voltage of $\sim 2\text{V}$. The color scale is the same as in Fig. 3. By comparison with images such as the one shown in Fig. 3, we infer the identity of the molecules in the domains as described in the caption to Fig. 3 and the text.







